

Accelerated Degradation Study of Highly Resistant Polymer Membranes for Energy and Environment Applications

Omkar Singh Kushwaha^{1,2}, Chilukuri Ver Avadhani^{1,2}, Namrata Singh Tomer³, Raj Pal Singh^{3*}

¹Polymer Science and Engineering Division, Council of Scientific and Industrial Research - National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 411008, India.

²Academy of Scientific and Innovative Research, 2, Rafi Marg, Anusandhan Bhavan, New Delhi – 110001, India.

³Bharati Vidyapeeth University, Advanced Research Centre in Pharmaceutical Sciences and Applied Chemistry, Erandawane, Pune - 411038, India.

^{1,2} os.kushwaha@ncl.res.in; ^{3*}rp.singh.ncl@gmail.com

Abstract

An accelerated photodegradation study was performed on poly (2,2'-butylene-5,5'-bibenzimidazole) (PBIB) and poly (2,2'-phenylene-5,5'-bibenzimidazole) (PBIP) membranes to study their stability and mechanism of photo-degradation. Polymer membranes were irradiated by polychromatic UV rays having $\lambda > 300$ nm and were characterized by FT-IR spectroscopy, WAXD, DSC, SEM and contact angle measurements.

Keywords

Degradation; Photo-Oxidation; Photo-Irradiation; Membranes; Stabilization; FT-IR spectroscopy

Introduction

The progress in polymer science and engineering has introduced thousands of new materials, and among them many polymers are found applicable in every promising research field such as space science, solar cells, fuel cells, electronics & communication, medical science and tissue engineering [Kumar et al. 2009; Rana et al. 2010; Kushwaha et al. 2013]. The high performance polymers (HPPs) such as Nafion and Polybenzimidazoles have attracted great attention of the researchers in green energy technologies, especially in fuel cells and gas separations [Kushwaha et al. 2014]. Polybenzimidazole membranes are mainly used for outdoor applications excluding recently reported applications in fuel cells and gas separations. The application of these HPPs as polymer electrolyte membranes (PEMs) for conduction of proton is very significant in the fuel cell performance and efficiency [Patrick et al. 2004]. Because of the advantages in synthesis, availability of raw materials, and high performance, the polybenzimidazoles are one of the

extensively researched polymers at present for fuel cell applications and gas separations. To enhance the properties of PBIs, various modifications have been adopted [Lobato et al. 2007, Chang et al. 2010]. The first cross-linking of polybenzimidazole [Gillham 1963] and use as adhesive [Litvak et al. 1968] to bond Stainless-Steel Beryllium and Titanium alloys has been reported. The first report on poly-electrolyte behaviour of PBI in formic acid [Kojima 1981] followed reports of its high thermal and chemical resistance. Since then, several publications reported potential applications of PBI for ion exchange membranes in reverse – osmosis [Sawyer et al. 1984], in catalysis [Li et al. 1985] and as high temperature laminates [Ramirez et al. 1985].

The First report on doped PBI as a new polymer electrolyte [Wainright et al. 1995] and the first report on the application of doped PBI in methanol and H₂O₂ fuel cells [Wainright et al. 1996; Wang et al. 1996] came in late 1990's. Since then hundreds of research papers and patents related to fuel cell applications of PBIs have been reported [Bai et al. 2011; Bose et al. 2011; Laberty-Robert et al. 2011; Peron et al. 2011; Yee et al. 2012; Fujigaya et al. 2013]. Several authors showed enhancement in the fuel cell performance and durability [Marestin et al. 2008; Kallitsis et al. 2009; Li et al. 2009]. Carbon based nanomaterials are also applied to reinforce and improve the performance of Nafion based fuel cells [Thomassin et al. 2007]. For the first time 50 % reinforcement in the mechanical properties of PBI by the incorporation of single-walled carbon nanotubes [Okamoto et al. 2008] was reported. The carbon reinforced composite materials showed high thermal resistance with the improved mechanical

properties [Okamoto et al. 2008; Rathod et al. 2009]. In order to find out the factors affecting durability of PBI membranes, thermal and chemical methods of membrane degradation were investigated [Chang et al. 2009; Li et al. 2009; Chang et al. 2010, Li et al. 2010; Daletou et al. 2010].

In the present study, we report the photodegradation of PBI membranes in order to find efficient and faster ways to determine service life of the membranes and also the factors affecting their stability and the mechanisms of degradation. The degradation studies were performed using polychromatic UV rays as a source of energy; enough for the scission of majority of chemical bonds which takes place via free radical generation [Kim et al. 1991; Moore et al. 1991]. In literature search, few publications report degradation studies performed on PBI based polymers, however photodegradation studies are rarely found.

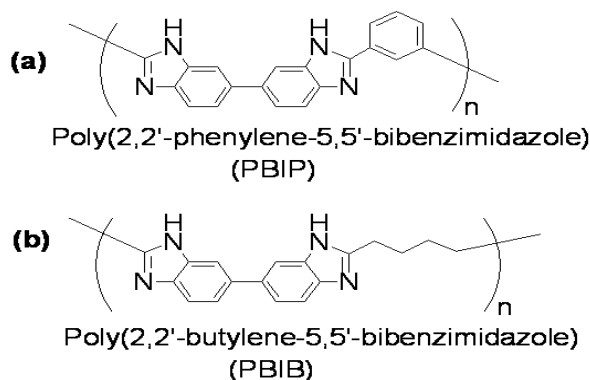


FIG.1 CHEMICAL STRUCTURES OF (a) PBIP AND (b) PBIB

To our best knowledge, this is the first comparative UV degradation study of polybenzimidazole membranes. UV irradiation gives expected degradation results in short interval of time [Andrews et al. 1978; Feldman et al. 2002; Lonkar et al. 2012]. The first photo-oxidative degradation study on isotactic polystyrene [Hrdlovic et al. 1971] and polystyrene polymers [Ikeda et al. 1978] gave the relationship between natural and accelerated degradations. Since then, photodegradation has been used as a strong tool to investigate the mechanism of degradation and lifetime expectancy of many polymers. The technique of photo-cross linking is reported by some research groups which are extensively utilized to modify the materials properties [Higuchi et al. 1991; Bauer et al. 1992]. Here, poly(2,2'-butylene-5,5'-bibenzimidazole) (PBIB) and poly(2,2'-phenylene-5,5'-bibenzimidazole) (PBIP) membranes (Figure 1) are investigated comparatively to analyze photodegradation and stabilization efficiencies.

Experimental

Materials

The polybenzimidazole polymer poly(2,2'-butylene-5,5'-bibenzimidazole) (PBIB) and poly(2,2'-phenylene-5,5'-bibenzimidazole) (PBIP) were received from Membranes and Separations Group, Council of Scientific and Industrial Research, CSIR-National Chemical Laboratory, India. The synthesis procedures and their properties have been described elsewhere [Bhavsar et al. 2010].

Membrane Casting And Photo-Irradiation

Membranes of ~ 50 μm thickness were cast on glass plate using Doctor's blade technique. For casting PBIP membranes, Dimethylacetamide (5% w/v) solutions were used whereas for PBIB membranes Formic acid (5% w/v) solutions were used. Dried solvents were used to prevent polymer precipitation. Polymer solutions were vacuum dried at 80 $^{\circ}\text{C}$ for 72 hours.

The thicknesses of polymer films were measured using Coating Thickness Gauge (Sheen SE1250FNP) by taking at least three measurements each time. Polymer films were dried in vacuum oven for 24 h at 80 $^{\circ}\text{C}$ before further studies.

For photo-degradation studies, samples of PBIB and PBIP (2 cm \times 4 cm) were irradiated by UV-rays having wavelength (λ) more than 300 nm. The UV- irradiation was done in SEPAP 12/24 instrument (manufactured by Materiel Physico Chimique, Neuilly, France) equipped with four 400 W low pressure mercury vapour lamps (Figure 2).

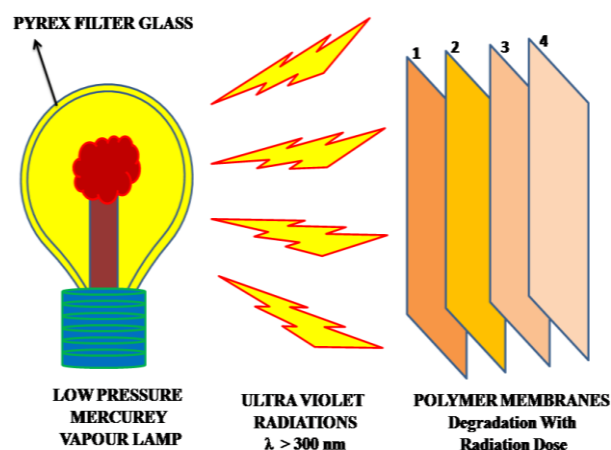


FIG. 2 DIAGRAMMATIC REPRESENTATION OF THE PHOTO-IRRADIATION PROCESS OF POLYMER MEMBRANES WITH POLYCHROMATIC UV RAYS.

Characterization And Measurements

PBI membranes were characterized using state of the

art facilities at the National Chemical Laboratory, Pune, India. For observing chemical changes occurred during UV-irradiation, attenuated total reflection/Fourier transform infrared (ATR/FT-IR) spectra of the membranes were recorded on GX Perkin Elmer spectrometer. ATR/FT-IR spectra were recorded in absorption mode with 32 scans each at a resolution of 4 cm^{-1} in the range of 4000 to 600 cm^{-1} . Wide Angle X-ray diffraction measurements were recorded on Rigaku Dmax 2500 diffractometer in the diffraction angle (2θ) range of 5° to 50° with a scan rate of 4° min^{-1} using Cu $K\alpha$ wavelength (1.54 \AA). Calorimetric measurements were performed on the DSC-Q10 TA instruments with heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen purge of 50 ml min^{-1} from $30\text{ }^\circ\text{C}$ to $420\text{ }^\circ\text{C}$ in sealed aluminium pans (sample size $2\text{--}4\text{ mg}$). The morphologies of the fresh and irradiated PBI membranes were studied by Quanta 200 3D Scanning Electron Microscopy (SEM) operated on low vacuum mode in the range of $0\text{--}200\text{ Pa}$ at 20 kV using Large Field Detector. The samples were sputter coated with 10 nm thick layer of gold by using a Polaron SC 6420 Sputter Coater for SEM measurements.

The hydrophilicity effects of UV-irradiation were studied by measuring Contact angles on RAME-HART NRL-Model CA goniometer fitted with Cannon camera. Computer inbuilt system software was used to determine the contact angles.

Results & Discussion

Chemical Structure And Photodegradation Products

The structure and morphology of PBI membranes have been described in great detail elsewhere [Bhavsar et al. 2010]. The chemical changes occurred due to photo irradiation of PBIB and PBIP samples are studied by FT-IR spectroscopy in absorption mode in the range of 3850 cm^{-1} to 600 cm^{-1} (Figure 3).

Figure 3a shows FTIR spectra of PBIB membranes obtained during 250 h of UV irradiation whereas Figure 3b shows FTIR spectra of PBIP membranes in the same duration. It is evident from the spectra that major changes occurred in the fingerprint region which tend to increase with the increase in UV irradiation time. The carbonyl region shows maximum changes which are attributed to the primary oxidation of PBI membranes. The expanded carbonyl spectra show the evolution of carbonyl peak with the irradiation time (Figure 4). It is clearly evident from the figure that the extent of the degradation observed

in PBIP is comparatively less than PBIB, especially in the carbonyl region from 1800 cm^{-1} to 1650 cm^{-1} .

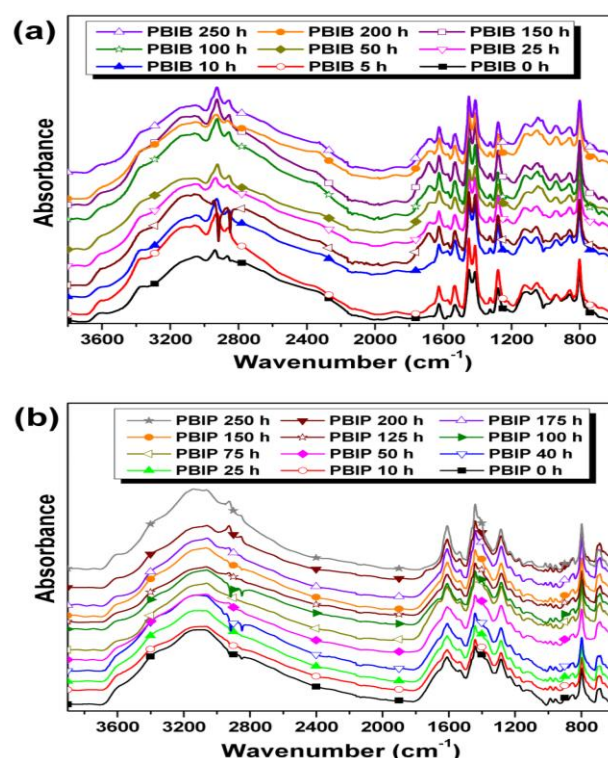


FIG. 3 FT-IR SPECTRA OF POLYMER MEMBRANES DURING PHOTO-IRRADIATION FROM 0 h to 250 h, (a) PBIB AND (b) PBIP. ARBITRARY ABSORBANCE IS USED FOR THE PURPOSE OF COMPARATIVE STUDY.

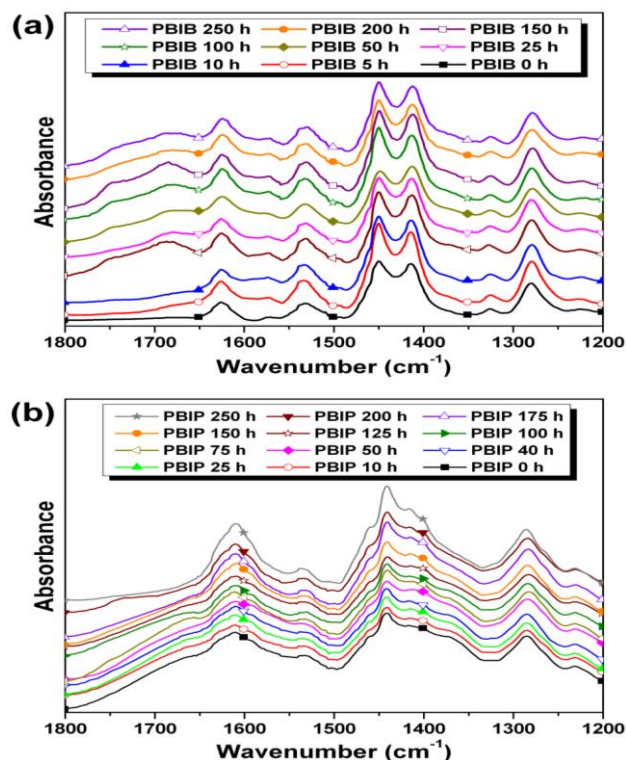


FIG. 4 FT-IR SPECTRA OF POLYMER MEMBRANES (FINGERPRINT REGION) DURING PHOTO-IRRADIATION OF (a) PBIB AND (b) PBIP. THE SPECTRA ARE PLOTTED USING ARBITRARY ABSORBANCE.

The higher absorbance in the carbonyl region indicates severe oxidative degradation. The broad peaks observed here are attributed to formation of several oxidation products due to oxidative photodegradation. It is clear from the above observations that the extent of oxidation is lesser in PBIP which is attributed to better chemical stability of PBIP over PBIB.

In order to investigate the photodegradation products, second derivatives of the respective FT-IR spectra [Windig et al. 1994; Prinos et al. 1998] are obtained (Figure 5). It is evident from the second derivatives of the FT-IR spectrum that both the PBIB and PBIP membranes are susceptible to the photodegradation and this process continued with the increase in UV irradiation time. It is also evident from the second derivatives that degradation is more intense in PBIB which is attributed to higher stability of PBIP over PBIB.

The formation of photo-degradation products may be recognized by their respective absorption frequencies.

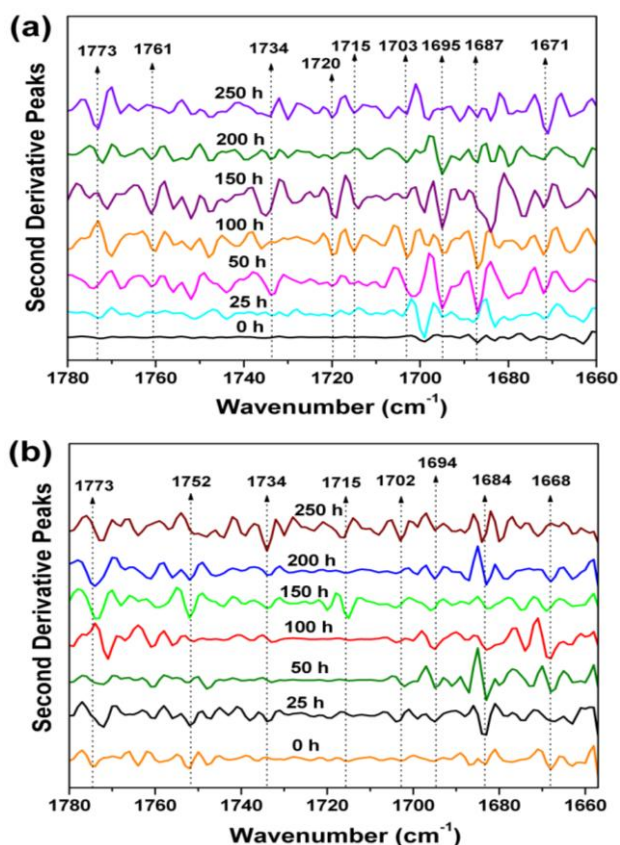


FIG. 5 SECOND DERIVATIVES OF FT-IR SPECTRUMS (IN CARBONYL REGION) OF (a) PBIB AND (b) PBIP MEMBRANES. THE SECOND DERIVATIVES OF INDIVIDUAL SPECTRUM ARE SHOWN IN ONE GRAPH USING ARBITRARY VALUES. CAPTIONS ARE PROVIDED TO EACH SECOND DERIVATIVE TO SHOW RESPECTIVE CHANGES TAKEN PLACE WITH THE POLYCHROMATIC UV-IRRADIATION TIME.

The peaks at higher frequencies such as 1695 cm^{-1} , 1703 cm^{-1} , 1715 cm^{-1} and 1720 cm^{-1} may be attributed to the formation of some carbonyl functional compounds like carboxylic acids and ketones [Ellaboudy et al. 1996; Siesler et al. 2011]. The peaks from 1723 cm^{-1} to 1747 cm^{-1} are attributed to the formation of the aldehydes and esters whereas those with higher frequencies above 1752 cm^{-1} are attributed to the formation of the aryl carbonates. The multiple curve fitting (MCF) of the photoirradiated FTIR spectrum of both membranes are plotted in Figure 6.

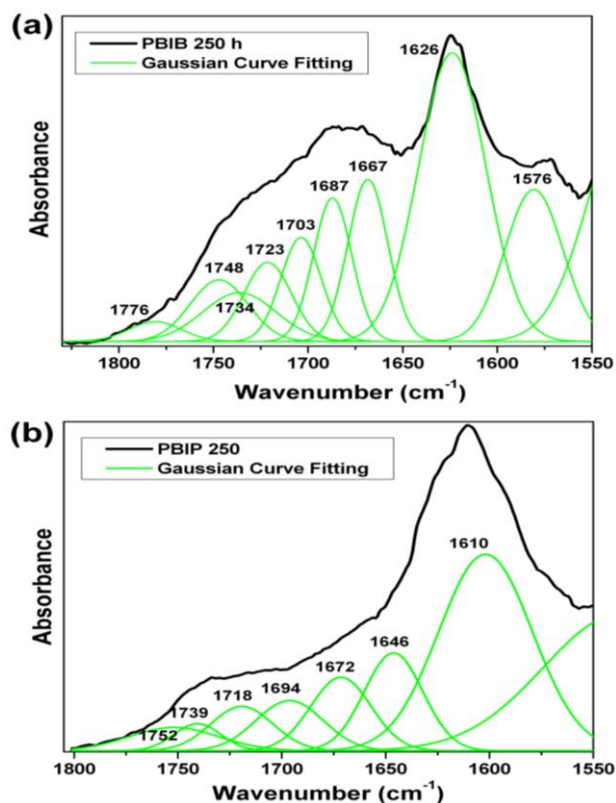


FIG. 6 GAUSSIAN CURVE FITTING OF FT-IR SPECTRUM OF (a) PBIB AND (b) PBIP MEMBRANES IN CARBONYL REGION TAKEN AFTER 250 h OF UV-IRRADIATION. THE MULTIPLE CURVE FITTING IS SHOWING THE DETAILED IR PEAKS.

In Figure 6, the intensity and absorption patterns may be easily observed, which are in agreement with the above findings and reveal the oxidative mechanism of degradation. The broad peaks appeared in the carbonyl region represent products with carbonyl ($\text{C}=\text{O}$) functionalities. The oxidation of PBIs with the UV irradiation time is reflected by the growth of the carbonyl indices (Figure 7) and hydroxyl indices (Figure 8). The following relationship is used to calculate carbonyl index (C. I.) [Subowo et al. 1986].

$$\text{C.I.} = \frac{\text{Absorption frequency at } 1700\text{ cm}^{-1}}{\text{Absorption frequency at } 3900\text{ cm}^{-1}}$$

The C. I. analysis shows an overall increase in the

carbonyl content of the polymers till 200 h of irradiation which slowed down later. Such chemical changes are attributed to oxidative photo-degradation.

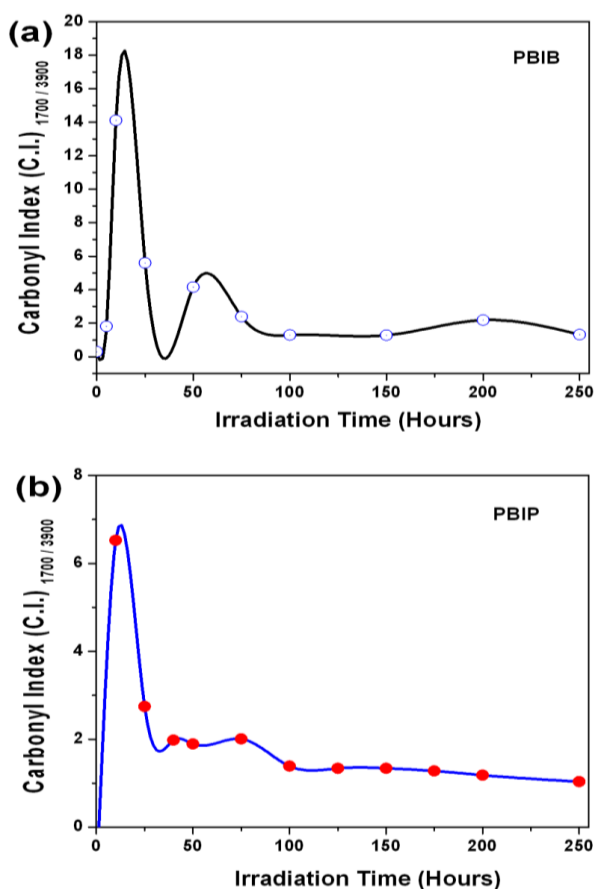


FIG. 7 THE CARBONYL INDICES OF (a) PBIB AND (b) PBIP WITH THE PHOTO-IRRADIATION.

The initial high C.I. is due to the oxidation of exposed surface of membrane which slows down after 50 h of irradiation. The high C.I. corresponds to high oxidation probability, hence the lower stability of the material. The PBI membranes are highly dense which delays oxidation of inner layers of membranes. It may also be noted that the oxidation of PBIB is faster as compared to the PBIP which is attributed to the compact structure and strong π - π stacking of PBIP membranes than those of PBIB. The aliphatic butylenes moiety in the PBIB polymer may comparatively provide the more susceptible sites of radical stabilization hence, increased oxidation.

Similarly, the appearance of various peaks in the hydroxyl region may be observed with the photoirradiation (Figure 2) and are clearly evident in the second derivative peaks of the respective FTIR spectrum (Figure 8).

The growth of some peaks of PBIB and PBIP are clearly visible whose absorbance depends on duration

of irradiation. The peaks at 3398 cm^{-1} , 3424 cm^{-1} , 3464 cm^{-1} , and 3494 cm^{-1} correspond to aromatic primary and secondary amines N-H stretching frequencies. The absorbance frequencies above 3500 cm^{-1} to 3700 cm^{-1} correspond to the formation of H-bonded and non H-bonded hydroxy groups [Musto et al. 1993].

$$\text{H.I.} = \frac{\text{Absorption frequency at } 3585 \text{ cm}^{-1}}{\text{Absorption frequency at } 3900 \text{ cm}^{-1}}$$

Similar to C. I., hydroxyl index (H. I.) also attributes to oxidation. The gradual increase in the hydroxyl content is observed (Figure 9). The hydroxyl index is calculated at 3585 cm^{-1} by using the given relationship [Meyer et al. 1991; Balagangadharan et al. 1992]. The gradual increase in the hydroxyl content during 250 h irradiation membranes is shown in Figure 9.

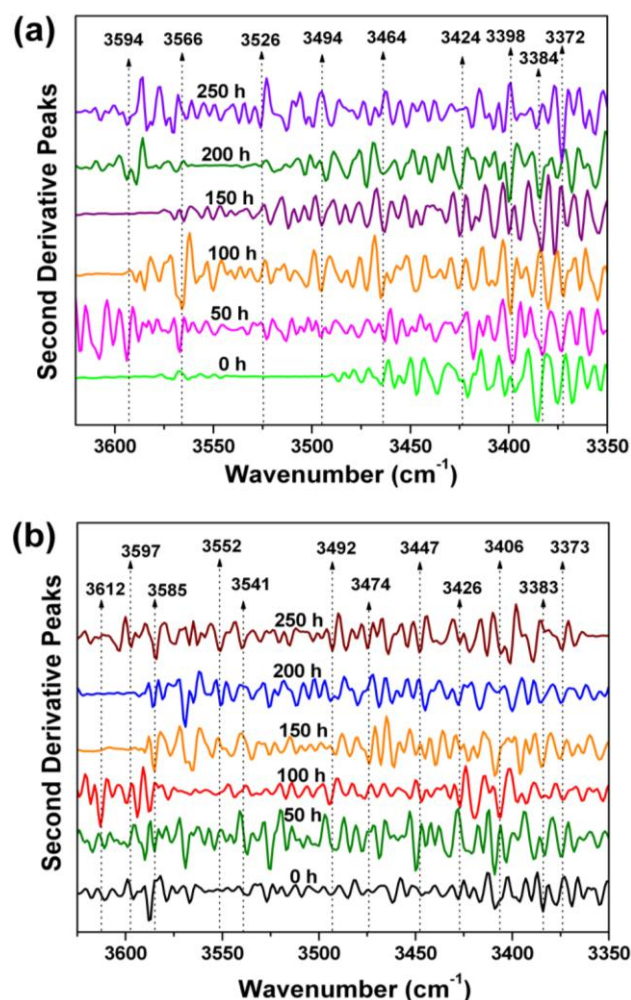


FIG. 8 SECOND DERIVATIVE OF FT-IR SPECTRUM OF (a) PBIB and (b) PBIP IN THE HYDROXYL REGION RANGING FROM 0 h TO 250 h OF PHOTO-IRRADIATION. THE SECOND DERIVATIVES OF INDIVIDUAL SPECTRUM ARE SHOWN IN ONE GRAPH USING ARBITRARY VALUES ON VERTICAL AXIS. CAPTIONS ARE PROVIDED TO EACH SECOND DERIVATIVE TO SHOW RESPECTIVE CHANGES TAKEN PLACE WITH THE POLYCHROMATIC UV-IRRADIATION TIME.

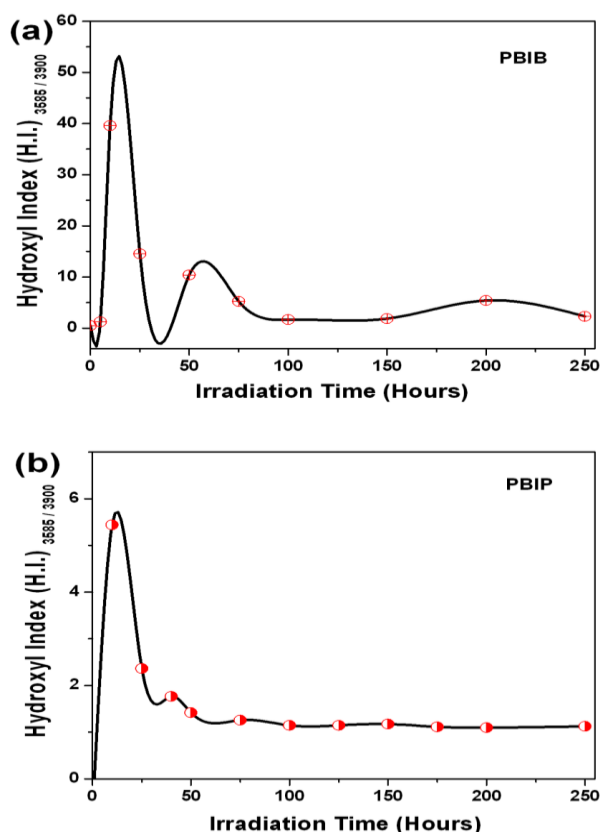


FIG. 9 HYDROXYL INDEX OF (a) PBIB AND (b) PBIP WITH PHOTO-IRRADIATION

TABLE 1 FT-IR ABSORPTION FREQUENCIES AND THE ASSIGNMENT OF RESPECTIVE PEAKS

Absorption Frequency (cm ⁻¹)	Peak Assignment
3620 – 3200	Hydroxy (–O–H stretching) Hydroperoxide (–O–O–H stretching)
3500 – 3400	Aromatic amine (N–H stretching)
1800 – 1700	Carbonyl (C=O stretching)
1715 – 1705	Carboxylic acid (C=O stretching)
1750 – 1735	Ester (C=O stretching)
1760 – 1735	Lactone (C=O stretching)
1725 – 1715	Ketone (C=O stretching)
1615 – 1450	Aromatic (C=C ring stretching)
3150 – 3050	Aromatic (C–H stretching)
3000 – 2800	Aliphatic (C–H stretching)
1150 – 1050	Ether (C–O–C stretching)

The hydroxyl index is calculated at 3585 cm⁻¹ by using following relationship [Meyer et al. 1991; Balagangadharan et al. 1992]. The obtained results are in agreement with the reported results of chemical and thermal degradation of the polymers with similar chemical structures. More importantly, it is evident that the present study gives faster and enhanced results of degradation. The peaks in the FT-IR spectra of both the polymers have been summarized in Table 1.

Glass Transition And Chain Packing

The DSC spectra of neat PBIB and PBIP polymers show T_g at 268 °C and 303 °C respectively (Figure 10).

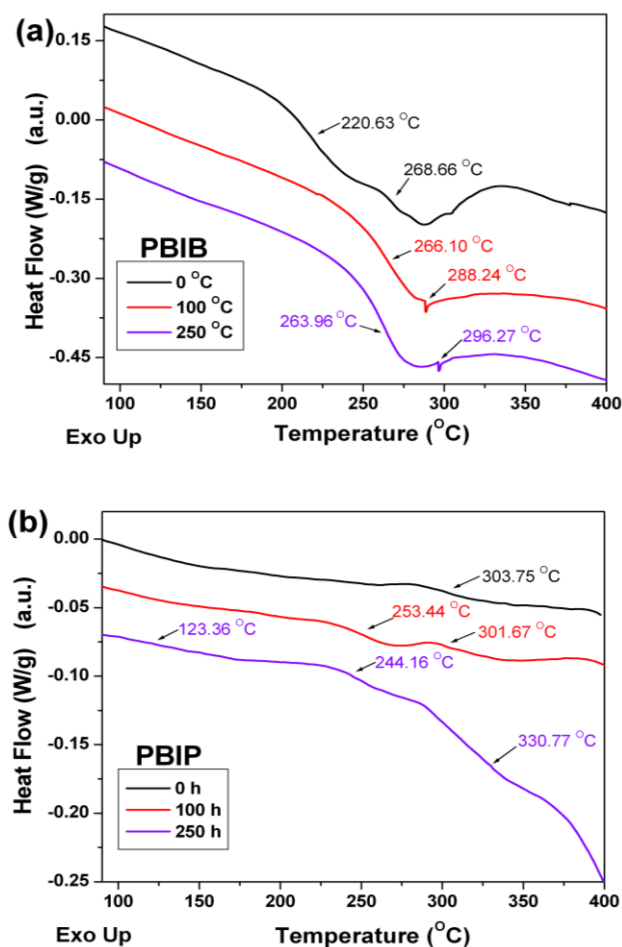


FIG. 10 DSC GRAPHS OF (a) PBIB (b) PBIP

The T_g of irradiated polymer samples gradually decreases with the irradiation time which may attributed to the preferred chain scissions than the cross linking of PBIs. In PBIP the T_g after 250 h of irradiation came down to 244 °C whereas in PBIB it decreased to 263 °C (Table 2).

TABLE 2 DSC MEASUREMENTS

Irradiation Time (h)	T_g PBIP (°C)	T_g PBIB (°C)
0	303	268
100	253	266
250	244	263

The rapid decrease in T_g of PBIP is attributed to the high absorbance of UV radiations because of high π -conjugated system whereas a weaker effect is observed in PBIB due to lack of strong π -conjugations. The decrease in T_g values may also be due to the destruction of π - π stacking of polybenzimidazole rings.

Hydrophilicity And Polar Functional Groups

The contact angle measurements are performed to find the surface energy changes and modifications occurred due to photoirradiation (Figure 11). The contact angle measurements of both polymers are measured (Figure 12) and summarized (Table 3) which reveal a regular decrease in contact angle of both the polymer samples with the UV irradiation time.

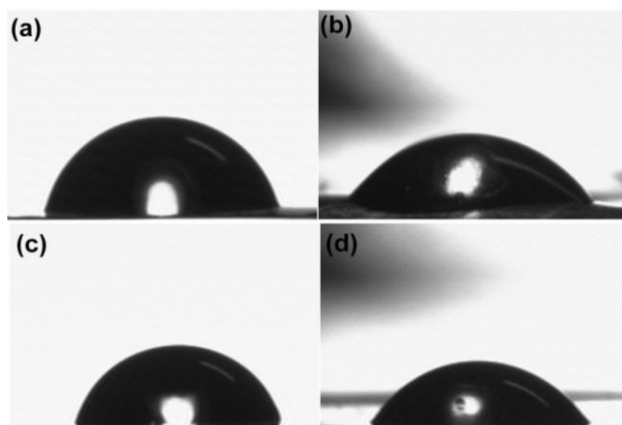


FIG. 11 IMAGES CAPTURED DURING CONTACT ANGLE MEASUREMENTS OF (a) PBIB (BEFORE PHOTO-IRRADIATION), (b) PBIB (AFTER 250 h PHOTO-IRRADIATION), (c) PBIP (BEFORE PHOTO-IRRADIATION) AND (d) PBIP (AFTER PHOTO-IRRADIATION)

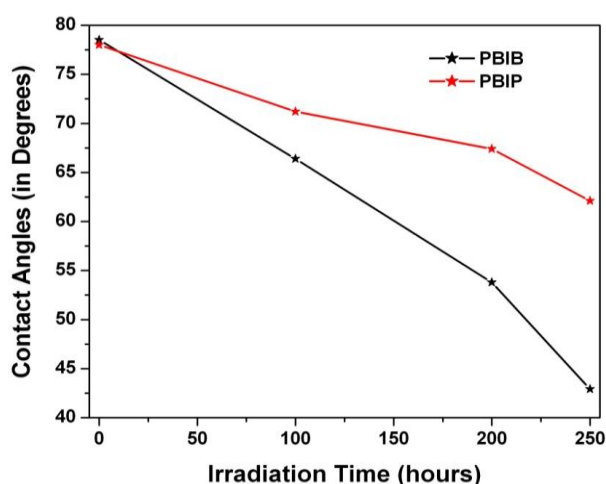


FIG. 12 GRAPHICAL REPRESENTATION OF CONTACT ANGLES OF PBIB AND PBIP

TABLE 3 CONTACT ANGLE MEASUREMENTS

Irradiation Time, (h)	Contact Angle of PBIB, (deg)	Contact Angle of PBIP, (deg)
0	78.5	78.0
100	66.4	71.2
200	53.8	67.4
250	42.9	62.1

In PBIB membrane the contact angle decreased from 78.5° to 42.9° whereas in PBIP it decreased from 78° to 62.1° which reveals that the surface damages occurred

due to UV irradiation are severe in PBIB samples as compared to PBIP. This may be attributed to the change in surface energy, morphology and chemical nature. It is attributed to the regular decrease in surface energies due to the photodegradation of polymers [Halperin et al.1992; Awaja et al. 2009].

The FTIR results further revealed the formation of hydrophilic hydroxyl, carboxylic as well as amino groups. After photoirradiation, all samples showed an increase in hydrophilic nature therefore, pretreatment of PBI membranes by UV rays may be useful in increasing water retention capacity for various applications.

Surface Degradation And Development Of Nanoscale Morphology

The SEM images of neat polymer samples show smooth surfaces whereas, photo irradiated samples of both polymer show the development of nano dimensional cracks (Figure13). The cracks are more severe in PBIB films as compared to PBIP. The width of these nano dimensional cracks is in the range of 35 nm to 200 nm with the length in few micrometers.

The SEM interpretations strongly support the FTIR and contact angle results. These membrane surface cracking occurred due partial change in the chemical structure of the used material. The oxidation due to prolonged irradiation resulted in the growth of fracture defects upto several micrometres. From the SEM results it is evident that UV irradiation process may also be used as a tool for nano patterning of PBI materials.

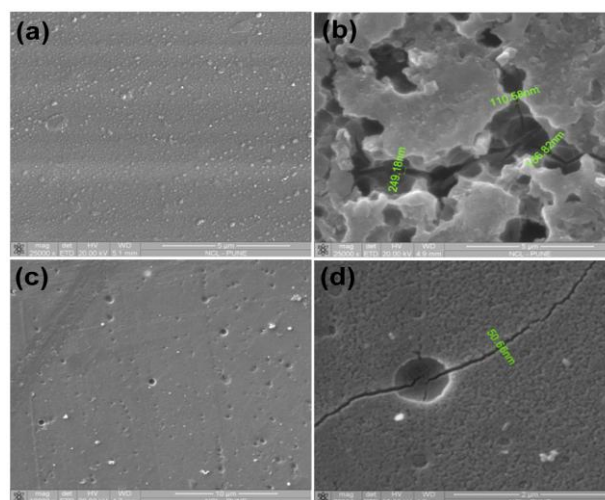


FIG. 13 SEM PICTURES CAPTURED DURING PHOTO-OXIDATIVE DEGRADATION STUDY OF (a) PBIB (BEFORE PHOTO-IRRADIATION), (b) PBIB (AFTER 250 H PHOTO-IRRADIATION), (c) PBIP (BEFORE PHOTO-IRRADIATION) AND (d) PBIP (AFTER PHOTO-IRRADIATION).

Amorphous Nature Of Membranes And Their Degradation

Wide angle X-ray diffraction study show broad diffraction peaks of polybenzimidazole samples (Figure 14) which are characteristic in amorphous polymers. The WAXD spectra of PBIB (Figure 14a) and PBIP (Figure 14b) are summarized in table 4.

TABLE 4 WAXD OBSERVATIONS

Irradiation Time (h)	2 θ (PBIB)	d_{sp} (PBIB)	2 θ (PBIP)	d_{sp} (PBIP)
0	19.9	4.45	23.8	3.74
150	22.5	3.96	24.0	3.68
250	22.8	3.90	24.4	3.64

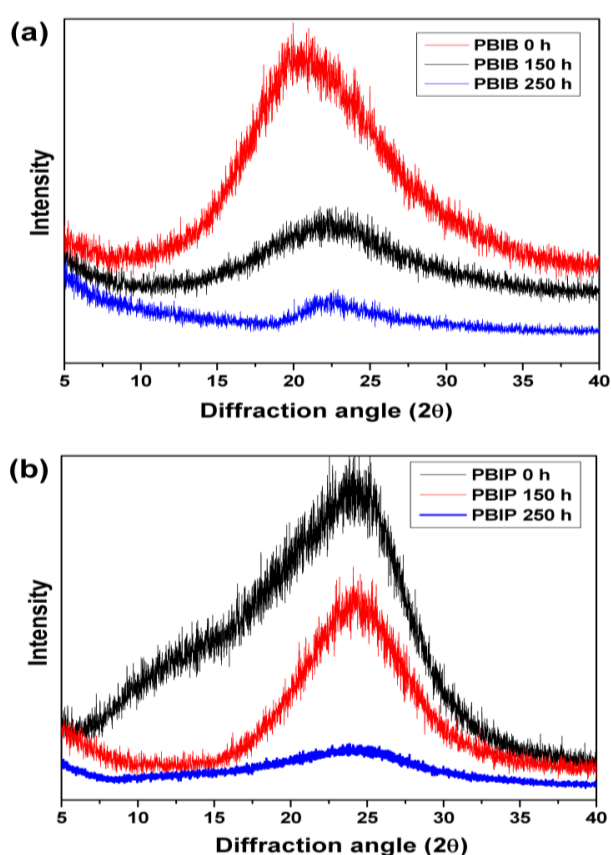


FIG. 14 WAXD OBTAINED DURING PHOTO-OXIDATIVE DEGRADATION OF (a) PBIB AND (b) PBIP

The decrease in intensity of these peaks may be observed as a result of photo degradation with the increase in diffraction angles. The diffraction angle is increased from 19.9° to 22.8° in PBIB whereas in PBIP it is increased from 23.8° to 24.4°. These changes may be attributed to the chain scissions taken place during photo-oxidative degradations [Kulshrestha et al. 2010].

The d-spacing values (d_{sp}) decreased in PBIB from 4.45 Å to 3.90 Å and in PBIP from 3.74 Å to 3.64 Å. This may be attributed to the shortning of polymer chains due to chain scissions occurred during photo-

oxidation. The WAXD results also revealed that PBIP membrane are more stable than PBIB.

Mechanism Of Degradation Of Polybenzimidazoles

The degradation investigations of PBI membranes accomplished by various characterization techniques which revealed pathway of photooxidative degradation in polybenzimidazole membranes. Based on the results obtained by ATR-FTIR spectroscopy, a general mechanism of photodegradation of PBIB and PBIP is proposed (Figure 15). The mechanism of photo-oxidative degradation may be initiated by the photo-activation of π e-(s) of unsaturated bonds which results in excited triplet state of polymer $^3(\pi-\pi)^*$ via free-radical generation.

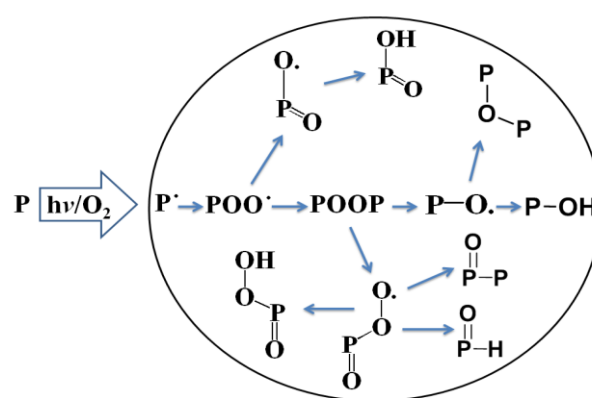


FIG. 15 GENERAL PHOTO-OXIDATIVE DEGRADATION MECHANISM OF PBI MEMBRANES

Subsequently, the reaction of $^3(\pi-\pi)^*$ polymer free radicals with $^3(\pi-\pi)$ molecular oxygen results in the oxidation of polymer with the formation of polymer oxy-radicals. These oxy-radicals upon rearrangements give rise to various oxidized products [Bressy et al. 2013]. As evidenced by FTIR spectroscopy observations, the degradation products are expected to be derivatives of mostly carboxylic acids, peroxides, ketones, aldehydes, ethers, esters, alcohols and phenols.

Conclusions

The accelerated degradation and the characterization of polybenzimidazole polymers have been demonstrated. The polybenzimidazole membranes subjected to oxidation upon UV irradiation. The FTIR results confirmed the oxidative mechanism of degradation of PBIB and PBIP membranes. The photodegradability was comparatively higher in PBIB when compared to PBIP. The conjugated aromatic structures provide more stability to aromatic polybenzimidazole polymers. The contact angle

measurements were in reasonable agreement with the FTIR results. The increase in hydrophilic nature of membranes confirmed the formation of polar groups. The SEM results revealed an increase in porosity of both membranes due the development of cracks and holes on polymer surface. The above findings are important from the perspectives of analysis of various membranes, their degradation and stabilization, and performance evaluation.

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REFERENCES

- Andrews, Edgar H. "The short and long term performance of polymers in different environments." *British Polymer Journal* 10, (1978): 39-46.
- Awaja, Firas, Michael Gilbert, Georgina Kelly, Bronwyn Fox, and Paul J. Pigram. "Adhesion of polymers." *Progress in polymer science* 34 (2009): 948-968.
- Bai, He, and WS Winston Ho. "Carbon dioxide-selective membranes for high-pressure synthesis gas purification." *Industrial & Engineering Chemistry Research* 50 (2011): 12152-12161.
- Balagangadharan, V. P., Korah Bina Catherine, K. G. Kannan, and K. N. Ninan. "Size exclusion chromatographic studies on the urethane reaction in hydroxyl-terminated polymers." *Polymer international* 29 (1992): 191-194.
- Bauer, D. R., D. F. Mielewski, and J. L. Gerlock. "Photooxidation kinetics in crosslinked polymer coatings." *Polymer degradation and stability* 38 (1992): 57-67.
- Bhavsar, Rupesh S., et al. "Polybenzimidazoles based on 3, 3'-diaminobenzidine and aliphatic dicarboxylic acids: Synthesis and evaluation of physicochemical properties toward their applicability as proton exchange and gas separation membrane material." *Journal of applied polymer science* 120 (2011): 1090-1099.
- Bose, Saswata, Tapas Kuila, Thi Xuan Hien Nguyen, Nam Hoon Kim, Kin-tak Lau, and Joong Hee Lee. "Polymer membranes for high temperature proton exchange membrane fuel cell: recent advances and challenges." *Progress in Polymer Science* 36 (2011): 813-843.
- Bressy, Christine, Van Giang Ngo, Fabio Ziarelli, and André Margailan. "New insights into the adsorption of 3-(trimethoxysilyl) propylmethacrylate on hydroxylated ZnO nanopowders." *Langmuir* 28 (2012): 3290-3297.
- Chang, Zhihong, Hongting Pu, Decheng Wan, Lu Liu, Junjie Yuan, and Zhenglong Yang. "Chemical oxidative degradation of Polybenzimidazole in simulated environment of fuel cells." *Polymer Degradation and Stability* 94 (2009): 1206-1212.
- Chang, Zhihong, Hongting Pu, Decheng Wan, Ming Jin, and Haiyan Pan. "Effects of adjacent groups of benzimidazole on antioxidation of polybenzimidazoles." *Polymer Degradation and Stability* 95 (2010): 2648-2653.
- Daletou, M. K., M. Geormezi, E. K. Pefkianakis, C. Morfopoulou, and J. K. Kallitsis. "Fully aromatic copolyethers for high temperature polymer electrolyte membrane fuel cells." *Fuel Cells* 10 (2010): 35-44.
- Ellaboudy, Ahmed S., Paul J. O'Connor, and James C. Tou. "Correlated electron spin-resonance and infrared spectroscopic study of the postformation auto-oxidation phenomenon in plasma-polymerized 4-vinyl pyridine films." *Journal of applied polymer science* 60 (1996): 637-647.
- Feldman, D. "Polymer weathering: photo-oxidation." *Journal of Polymers and the Environment* 10 (2002): 163-173.
- Fujigaya, Tsuyohiko, and Naotoshi Nakashima. "Fuel Cell Electrocatalyst Using Polybenzimidazole-Modified Carbon Nanotubes As Support Materials." *Advanced Materials* 25 (2013): 1666-1681.
- Gillham, J. K. "Polymer structure: cross-linking of a polybenzimidazole." *Science* 139 (1963): 494-495.
- Halperin, A., M. Tirrell, and T. P. Lodge. Book chapter "Tethered chains in polymer microstructures." In *Macromolecules: Synthesis, Order and Advanced Properties*, Advances in Polymer Science 31-71. Springer Berlin Heidelberg, 1992.
- Higuchi, Hiroyuki, Takashi Yamashita, Kazuyuki Horie, and Itaru Mita. "Photo-cross-linking reaction of benzophenone-containing polyimide and its model compounds." *Chemistry of Materials* 3 (1991): 188-194.

- Hrdlovic, P., J. Pavlinec, and H. H. G. Jellinek. "Degradation of polymers and morphology: Photo-oxidative degradation of isotactic polystyrene in presence of sulfur dioxide as function of polymer crystallinity." *Journal of Polymer Science Part A-1: Polymer Chemistry* 9 (1971): 1235-1245.
- Ikeda, Tomiki, Koji Kawaguchi, Hitoshi Yamaoka, and Seizo Okamura. "Photo-and Radiation-Induced Degradation of Vinyl Polymers in Solution. 2. Photosensitized Degradation of Poly- α -methylstyrene by Benzophenone." *Macromolecules* 11 (1978): 735-739.
- Kallitsis, Joannis K., Maria Georzezi, and Stylianos G. Neophytides. "Polymer electrolyte membranes for high-temperature fuel cells based on aromatic polyethers bearing pyridine units." *Polymer International* 58 (2009): 1226-1233.
- Kim, S. S., R. H. Liang. "Radiation effects on polymers." ACS symposium series, vol. 475, p. 135. 1991.
- Kojima Takakazu. "Polyelectrolyte Behavior of a Polybenzimidazole in Formic Acid." *Polymer Journal* 13 (1981): 85-87.
- Kulshrestha, Vaibhav, et al. "Microstructure change in poly (ethersulfone) films by swift heavy ions." *Micron* 41 (2010): 390-394.
- Kumar, Annamalai Pratheep, Dilip Depan, Namrata Singh Tomer, and Raj Pal Singh. "Nanoscale particles for polymer degradation and stabilization—trends and future perspectives." *Progress in Polymer Science* 34 (2009): 479-515.
- Kushwaha, Omkar S., C. V. Avadhani, and R. P. Singh. "Effect of UV rays on degradation and stability of high performance polymer membranes." *Advanced Materials Letters* 5 (2014): 272-279.
- Kushwaha, Omkar S., C. V. Avadhani, and R. P. Singh. "Photo-oxidative degradation of polybenzimidazole derivative membrane." *Advanced Materials Letters* 4 (2013): 762-768.
- Laberty-Robert, C., K. Valle, F. Pereira, and C. Sanchez. "Design and properties of functional hybrid organic-inorganic membranes for fuel cells." *Chemical Society Reviews* 40 (2011): 961-1005.
- Li, Nai-Hong, and Jean MJ Fréchet. "Polybenzimidazole-supported heterogeneous palladium catalysts." *Journal of the Chemical Society, Chemical Communications* 16 (1985): 1100-1101.
- Li, Q. F., Hans Christian Rudbeck, Andreas Chromik, Jens Oluf Jensen, Chao Pan, Thomas Steenberg, Martin Calverley, N. J. Bjerrum, and Jochen Kerres. "Properties, degradation and high temperature fuel cell test of different types of PBI and PBI blend membranes." *Journal of Membrane Science* 347 (2010): 260-270.
- Li, Qingfeng, Jens Oluf Jensen, Robert F. Savinell, and Niels J. Bjerrum. "High temperature proton exchange membranes based on polybenzimidazoles for fuel cells." *Progress in Polymer Science* 34 (2009): 449-477.
- Litvak, S. "Polybenzimidazole adhesives for bonding stainless steel, beryllium and titanium alloys. Pt. 1. Adhesive performance of PBI." *Adhes. Age* 11 (1968): 17-24.
- Lobato, Justo, Pablo Canizares, Manuel A. Rodrigo, and José J. Linares. "PBI-based polymer electrolyte membranes fuel cells: temperature effects on cell performance and catalyst stability." *Electrochimica Acta* 52 (2007): 3910-3920.
- Lonkar, Sunil P., Omkar S. Kushwaha, Andreas Leuteritz, Gert Heinrich, and R. P. Singh. "Self photostabilizing UV-durable MWCNT/polymer nanocomposites." *RSC Advances* 2 (2012): 12255-12262.
- Marestin Catherine, Gebel Gérard, Diat Olivier, Mercier Régis. "Sulfonated Polyimides." *Fuel Cells II, Advances in Polymer Science Volume* 216, 2008, pp 185-258.
- Meyer, Glenn A., Richard T. Lostritto, and Julian F. Johnson. "Characterization of hydroxypropylcellulose-indomethacin grafts as a function of molecular weight." *Journal of applied polymer science* 42 (1991): 2247-2253.
- Moore, J. A., Jin O. Choi, R. L. Clough, and S. W. Shalaby. "Radiation effects on polymers." ACS symposium series, vol. 475, p. 156. 1991.
- Musto, P., F. E. Karasz, and W. J. MacKnight. "Fourier transform infra-red spectroscopy on the thermo-oxidative degradation of polybenzimidazole and of a polybenzimidazole/polyetherimide blend." *Polymer* 34 (1993): 2934-2945.
- Okamoto, Minoru, Tsuyohiko Fujigaya, and Naotoshi Nakashima. "Design of an Assembly of Poly (benzimidazole), Carbon Nanotubes, and Pt

- Nanoparticles for a Fuel-Cell Electrocatalyst with an Ideal Interfacial Nanostructure." *Small* 5 (2009): 735-740.
- Okamoto, Minoru, Tsuyohiko Fujigaya, and Naotoshi Nakashima. "Individual Dissolution of Single-Walled Carbon Nanotubes by Using Polybenzimidazole, and Highly Effective Reinforcement of Their Composite Films." *Advanced functional materials* 18 (2008): 1776-1782.
- Patrick, John W. "Handbook of fuel cells. Fundamentals technology and applications: Edited by Wolf Vielstich, Arnold Lamm, Hubert A. Gasteiger; John Wiley and Sons Ltd, Chichester, England, (2004): 623.
- Peron, Jennifer, Zhiqing Shi, and Steven Holdcroft. "Hydrocarbon proton conducting polymers for fuel cell catalyst layers." *Energy & Environmental Science* 4 (2011): 1575-1591.
- Prinos, J., D. Bikiaris, S. Theologidis, and C. Panayiotou. "Preparation and characterization of LDPE/starch blends containing ethylene/vinyl acetate copolymer as compatibilizer." *Polymer Engineering & Science* 38 (1998): 954-964.
- Ramirez, J. E., and CF DWIGGINS. "high-temperature papers made of polybenzimidazole." *Tappi Journal* 68 (1985): A12-A14.
- Rana, V. K., Omkar S. Kushwaha, RajPal Singh, Satyendra Mishra, and Chang-Sik Ha. "Tensile properties, cell adhesion, and drug release behavior of chitosan-silver-gelatin nanohybrid films and scaffolds." *Macromolecular Research* 18 (2010): 845-852.
- Rathod, Dhanraj, Meenu Vijay, Nazrul Islam, Ramaiyan Kannan, Ulhas Kharul, Sreekumar Kurungot, and Vijayamohanan Pillai. "Design of an "all solid-state" supercapacitor based on phosphoric acid doped polybenzimidazole (PBI) electrolyte." *Journal of applied electrochemistry* 39 (2009): 1097-1103.
- Sawyer, L. C., and R. S. Jones. "Observations on the structure of first generation polybenzimidazole reverse osmosis membranes." *Journal of membrane science* 20 (1984): 147-166.
- Siesler, Heinz W. "Vibrational spectroscopy of polymers." *International Journal of Polymer Analysis and Characterization* 16 (2011): 519-541.
- Subowo, Wiwik S., M. Barmawi, and Oei Ban Liang. "Growth of carbonyl index in the degradation of polypropylene by UV irradiation." *Journal of Polymer Science Part A: Polymer Chemistry* 24 (1986): 1351-1362.
- Thomassin, Jean-Michel, Jozef Kollar, Giuseppe Caldarella, Albert Germain, Robert Jérôme, and Christophe Detrembleur. "Beneficial effect of carbon nanotubes on the performances of Nafion membranes in fuel cell applications." *Journal of Membrane Science* 303 (2007): 252-257.
- Wainright, J. S., J-T. Wang, D. Weng, R. F. Savinell, and M. Litt. "Acid-Doped Polybenzimidazoles: A New Polymer Electrolyte." *Journal of the Electrochemical Society* 142 (1995): L121-L123.
- Wainright, Jesse S., Jiang-tao Wang, and Robert F. Savinell. "Direct methanol fuel cells using acid doped polybenzimidazole as a polymer electrolyte." In *Energy Conversion Engineering Conference, 1996. IECEC 96., Proceedings of the 31st Intersociety, vol. 2, 1107-1111.*
- Wang, J-T., R. F. Savinell, J. Wainright, M. Litt, and H. Yu. "A H₂O₂ fuel cell using acid doped polybenzimidazole as polymer electrolyte." *Electrochimica Acta* 41 (1996): 193-197.
- Windig, Willem. "The use of second-derivative spectra for pure-variable based self-modeling mixture analysis techniques." *Chemometrics and intelligent laboratory systems* 23 (1994): 71-86.
- Yee, R. S. L., R. A. Rozendal, K. Zhang, and B. P. Ladewig. "Cost effective cation exchange membranes: A review." *Chemical Engineering Research and Design* 90 (2012): 950-959.



Prof. R. P. Singh is a distinguished scientist at Bharati Vidyapeeth Deemed University, Advanced Research Centre in Pharmaceutical Sciences & Applied Chemistry, Poona College of Pharmacy, Pune, India. Earlier he has served CSIR-National Chemical Laboratory, Pune as a scientist for thirty years in Polymer Science & Engineering Division, Pune, India. He has published more than 160 research papers and 20 US patents. He is a General Secretary of "The Society for Polymer Science (SPSI), India". His area of research includes bio-nanocomposites, biodegradable polymers, drug delivery, tissue culture, pharmaceutical polymers and degradation of polymer membranes.



O. S. Kushwaha is a UGC-Senior Research Fellow at Polymer Science & Engineering Division, CSIR-National Chemical Laboratory, Pune and Academy of Scientific and Innovative Research (AcSIR), New Delhi, India since 2009. He obtained his B. Sc. degree in Chemistry & Botany (2004)

and M.Sc. degree in Chemistry (2008) from Chhatrapati Shahu Ji Maharaj University (CSJMU), Kanpur. He has more than 12 years of teaching and research experience with several research papers published in international journals. He works on degradation-stabilization and structure-property relationship of biopolymers, polymer nanocomposites and high performance polymers.